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ORIGINAL ARTICLE

Kinetics of reduction leaching of manganese dioxide ore with *Phytolacca americana* in sulfuric acid solution

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KEYWORDS

Manganese dioxide ore;
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Abstract The leaching kinetics of reductive leaching of manganese from manganese dioxide ores (MDO) in dilute sulfuric acid in the presence of *Phytolacca americana* powder (PAP) was investigated. The effects of stirring speed, leaching temperature and leaching time, particle size, weight ratio of PAP to MDO (C_W) and sulfuric acid concentration (C_H) on the leaching efficiency of manganese were studied. The leaching efficiency of manganese based on the shrinking core model was found to be controlled by diffusion through the ash/inert layer composed of the associated minerals. The apparent activation energy is 15.18 kJ mol^{-1}. The experimental results indicate reaction order of 0.797 for C_H and 1.25 for C_W. The overall leaching efficiency equations for MDO dissolution reaction with PAP in dilute sulfuric acid were proposed by a semi-empirical model.

1. Introduction

Manganese is widely used in numerous fields, such as steel production, nonferrous metallurgy, batteries and fine chemicals [1,2]. Manganese dioxide is stable under both acidic and alkaline oxidizing conditions, so the extraction of manganese from manganese dioxide ores (MDO) must be carried out under reducing conditions [3].

Generally, MDO can be treated by roasting reduction-acid leaching and direct reduction leaching in H_2SO_4 or HCl solution [4,5]. The reductants in H_2SO_4 solution include H_2O_2 [6,7], $H_2C_2O_4$ [8], $FeSO_4$ [9], and SO_2 [10,11], while the reductive agents in HCl solution include nickel matter and H_2O_2 [2,12]. Recently, there are also a number of reports about using biomass as reductant to leach MDO [13,4,14–16].

Meanwhile, a comprehensible understanding of the leaching kinetics is necessary for an efficient design of leaching manganese ore [17]. Previous research on the leaching efficiency of MnO_2 with Fe^{2+} in H_2SO_4 solution is controlled by chemical reaction with the apparent activation energy (E_a) of 28 kJ·mol^{-1} [18]. Vegliò et al. [19] investigated leaching in

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lactose-sulfuric acid follows a shrinking core model with variable E_a. Likewise, Lasheen et al. [20] concluded that the leaching kinetics of MDO with molasses in HNO_3 is controlled by diffusion through the inner layer with E_a of 27.5 kJ·mol^{-1}. Similarly, Su et al. [21] asserted leaching kinetics of MDO with molasses alcohol wastewater in H_2SO_4 follows a shrinking core model with E_a of 57.5 kJ·mol^{-1}. Recently, there are some reports [22,23] on colloidal MnO_2, for the water-soluble colloidal MnO_2 plays an important role in surface chemistry, molecular sieves, catalysis, ion-exchange, biosensor and particularly energy storage. Khan et al. [23] examined the reduction of colloidal MnO_2 by ascorbic acid and concluded that the kinetics of the reduction reaction is second-order according with Eyring equation model. The kinetics of the reduction of water-soluble colloidal manganese dioxide by glycyl-leucine (Gly-Leu) follows the Arrhenius and Eyring equations over the range of temperatures used and different activation parameters [24].

However, the presence of these reducing agents of high cost, large amount leaching slag, environmental pollution, regional limitation of the biomass and other defects, hinders their wide application in metal manganese industry. Therefore, finding a new reductant is a key problem in the reductive leaching of MDO. *Phytolacca americana* is a perennial weed that occurs worldwide. It can grow fast in metalliferous fields and accumulate high Mn levels of approximately 19,300 μg·g^{-1} Mn in shoot dry matter in its leaves [25]. On the other hand, some researches of *P. americana* have been studied [26,27]. However, there is no report on the reduction of MnO_2 by *P. americana* available in the literature. Apart from starch the three major constituents in *P. americana* are cellulose, hemicellulose and lignin, which could be hydrolyzed into reductive carbohydrates in acid solution, such as glucose [28]. Therefore, *P. americana* can be applied to the reductive leaching of MDO in sulfuric acid solution. It may be a promising green process of reductive leaching of MDO, phyto-extraction of manganese from contaminated soils and remediation of contaminated soils of manganese mining area [29,30].

In this work, the reductive leaching of manganese from MDO by *P.americana* branch powder (PAP) was investigated. The effects of the main system variables on the leaching efficiency of manganese were examined. The kinetic model of a semi-empirical equation was determined.

2. Materials and methods

2.1. Characterization of materials

MDO were obtained from an electrolytic manganese company, situated in the western Hunan province, China. The ores were crushed and ground. The samples were sieved into four size fractions. Average particle size expressed as volume mean diameter d(4,3) is 63, 76, 122 and 204 μm by laser particle sizer (Mastersizer 2000, Malvern, UK). Sample characterization by XRD showed the presence of variety of metallic minerals including pyrolusite, manganosite, hausmannite, and gangue consisting primarily of quartz, kyanite, bauxite and hematite. Manganese compounds analyzed by XRD disappear after the leaching process. The ore was chemically analyzed for its major and minor elements listed in Table 1. *P. americana* were ground to the required particle size of −150 μm. The proximate analysis of PAP is shown in Table 2.

2.2. Experiment procedure

The leaching experiments were carried out with varying amounts of PAP portions of 10 g ore added into aqueous sulfuric acid solution in a closed glass flask. The ore slurry was then agitated at the required temperature for a specified reaction time in a thermostatically controlled water bath. Manganese concentration during the leaching process was estimated using Shimadzu UV–Vis spectroscopy at 525 nm [31]. Leaching efficiency was calculated by referring the amount of leached manganese in the liquor to its original input quantity.

2.3. Leaching kinetic models

The experimental data were correlated to the shrinking core models to obtain the kinetic equation. The shrinking core models previously analyzed by some authors [21,32] are as follows:

$$1-\frac{2}{3}X-(1-X)^{\frac{2}{3}}=\frac{2M_sD_{Aeff}C_{A0}}{a\rho_s r_0^2}t=k_dt \quad (1)$$

$$1-(1-X)^{\frac{1}{3}}=\frac{M_sk_c}{a\rho_s r_0}C_{A0}t=k_rt \quad (2)$$

$$1-(1-X)^{\frac{1}{3}}+\frac{y}{6}[(1-X)^{\frac{1}{3}}+1-2(1-X)^{\frac{2}{3}}]=kt \quad (3)$$

where X is the fraction reacted; k_d, k_r and k are rate constants, respectively; t is the reaction time. Eq. (1) is applicable to a diffusion-controlled process through the inner layer; Eq. (2) is a chemical reaction controlled process; Eq. (3) is a mixed controlled process (a combination of surface reaction and diffusion).

The temperature dependence of the reaction rate constant can be calculated by the Arrhenius equation:

$$k=A\exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

where A is frequency factor, E_a is activation energy of the reaction, R is universal gas constant, and T is absolute temperature.

3. Results and discussions

3.1. Effect of stirring speed

The effect of stirring speed on leaching efficiency was examined in the range of 200–700 r·min^{-1} under the conditions of 63 μm particle size, weight ratio of PAP to MDO (C_W) of

Table 1 Major chemical composition of manganese dioxide ore.

Composition	Mn	Fe	SiO_2	Al_2O_3	K_2O	CaO	MgO
Content (wt.%)	20.34	10.46	37.22	8.38	1.09	0.73	0.78

Table 2 Proximate analysis of *Phytolacca americana* branch powders.

Proximate analysis (%)	Methods for determination	Biomass constituent (%)	Methods for determination
Moisture 25.67	GB/T 2677.2-93	Cellulose 12.64	The hydrolysis of 72% H_2SO_4
Volatiles 65.38	YB/T 5189-2007	Hemicellulose 14.24	The hydrolysis of 2 mol L^{-1} HCl
Ash 4.7	GB/T 2677.3-93	Lignin 30.78	GB/T 2677.8-94

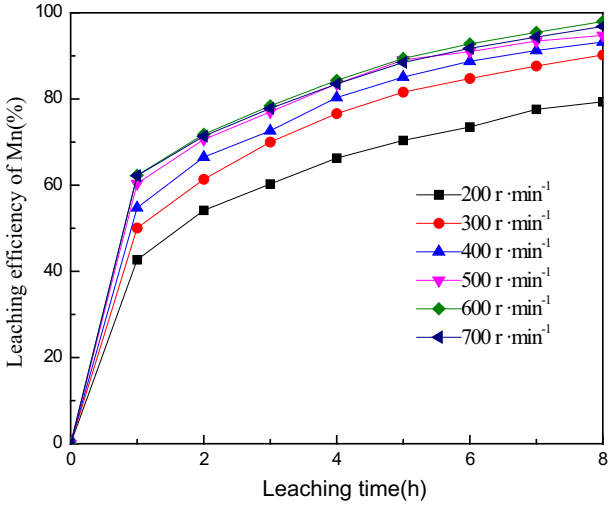

Figure 1 Effect of stirring speeds on the leaching efficiency of manganese.

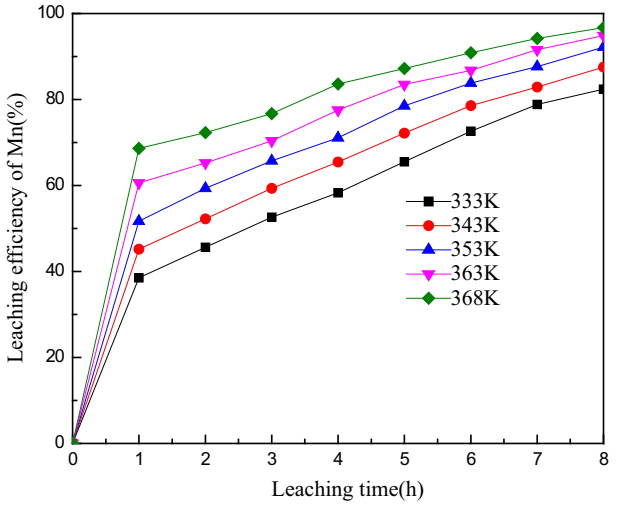

Figure 2 Effect of time and temperature on the leaching efficiency of manganese.

4–10 g, 1.7 mol·L^{-1} H_2SO_4 and 368 K. Results are shown in Fig. 1. The leaching efficiency increased with increasing stirring speed up to 400 r·min^{-1}. An increase in stirring speed usually increases the reductive leaching of manganese due to the suspension of the mineral particles and decreases the thickness of the mass transfer boundary layer on the surface of the particle [33]. The recovery of manganese was almost constant by increasing the stirring speed over 400 r·min^{-1}. Thus, a stirring speed of 400 r·min^{-1} was used thereafter to assure that the leaching reaction was not under external diffusion control.

3.2. Effect of leaching temperature and leaching time

The effect of leaching temperature was studied in the range of 333–368 K for a specified reaction time under the conditions of 63 μm particle size, C_W of 4–10 g, 1.7 mol·L^{-1} H_2SO_4 and 400 r·min^{-1}. The results, presented in Fig. 2, indicate that the leaching efficiency of manganese reached 96.47% at 368 K when the leaching time increased 8 h. With further increasing the leaching temperature and leaching time, the leaching rate of manganese increases slowly. This is because the final concentration of reagents reduces when the leaching reactions proceed with the increase of leaching time.

Of all the three models tested, all the studied data were found only to fit the relation in the Eq. (1) with correlation coefficients (R^2) greater than 0.9860. The linear relationship between Eq. (1) and leaching time (t) shown in Fig. 3 suggests that the leaching efficiency of manganese is controlled by diffusion through the ash/inert solid layer. Hence, the insoluble oxide minerals (quartz, hematite, etc.) associated with MDO may act as the ash/inert layer [7,20].

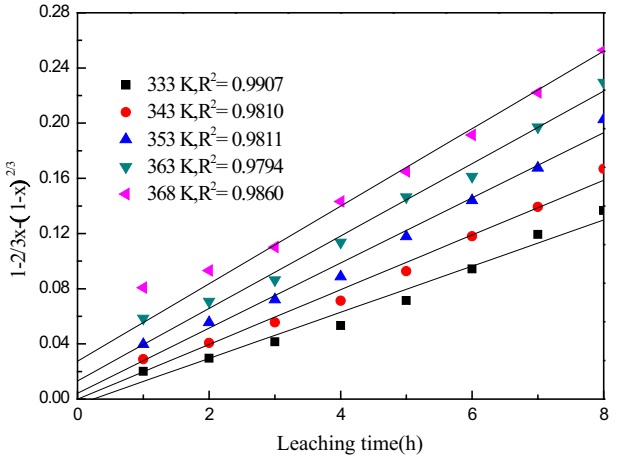

Figure 3 Variation of $1-\frac{2}{3}X-(1-X)^{2/3}$ with leaching time at various temperatures.

The apparent rate constant (k_d) was calculated as slopes of the straight lines summarized in Fig. 3. To calculate the activation energy, the Arrhenius plot of this leaching process is plotted using the values of $\ln k_d$ versus 1000/T with the R^2 of 0.9927. The slope of the line is −1.827. The activation energy in the temperature range between 333 K and 368 K was calculated to be 15.18 kJ·mol^{-1}. This value (< 40 kJ·mol^{-1}) clearly confirms that the leaching process is controlled by inner diffusion mechanism [34].

3.3. Effect of initial particle size of MDO

The effect of initial particle size of MDO was investigated under the conditions of C_W of 4–10 g, 1.7 mol·L^{-1} H_2SO_4, 400 r·min^{-1} and 368 K. Results are summarized in Fig. 4. The results from Fig. 4 show that the smaller the ore particle size, the faster was the manganese leaching. This was attributed to the effect of increased reaction-surface area of manganese minerals. It seemed that grinding was beneficial in terms of higher manganese extraction. However, this is limited by technical and economical reasons. Therefore, initial particle size of 63 μm was used in the remaining experiments. This conclusion was also supported by Raza et al. [35] and Zhu et al. [36].

In order to clarify the quantitative relationship between the reaction rate and particle size, initial data of MDO particle were analyzed in terms of Eq. (1). Eq. (1) fitted the data best for the range of the initial data with R^2 of 0.9853. Leaching kinetics constant varied with the inverse square of initial particle size for diffusion-controlled reactions in Eq. (1). Fig. 5 shows the quantitative relationship between the apparent rate constant (k_d) and particle size (r_0^{-2}), indicating the linear relationship between k_d and r_0^{-2} with R^2 of 0.9974. It is also affirmed that the leaching of MDO with PAP is controlled by the diffusion of reactant through the ash/inert solid layer [37].

3.4. Effect of weight ratio of PAP to MDO

The effect of C_w in the range of 1:10–5:10 was studied under the conditions of 1.7 mol·L^{-1} H_2SO_4, 63 μm, 400 r·min^{-1} and 368 K. Results are shown in Fig. 6. As can be seen from Fig. 6, the leaching efficiency of manganese increased with an increasing of C_w, but it became slow with further increase to 4:10 at which above 98.57% recovery of manganese was obtained within 8 h. This is supported by other studies [8,38].

The results were also applied to Eq. (1) and k_d values for each weight ratio of PAP to MDO were determined. There is a good linear relationship between Eq. (1) and leaching time

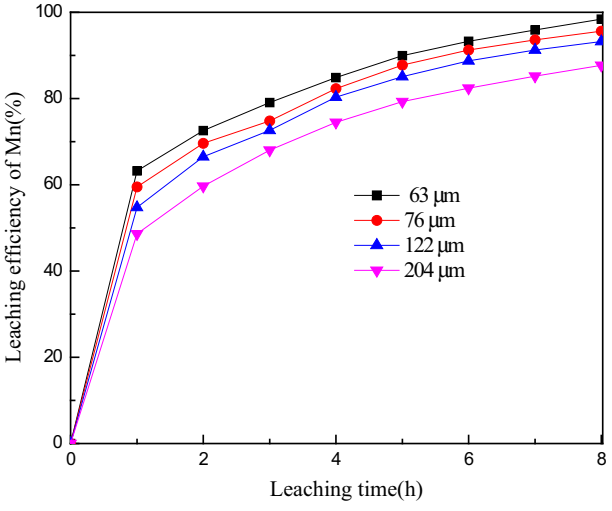

Figure 4 Effect of MDO particle size on the leaching efficiency of manganese.

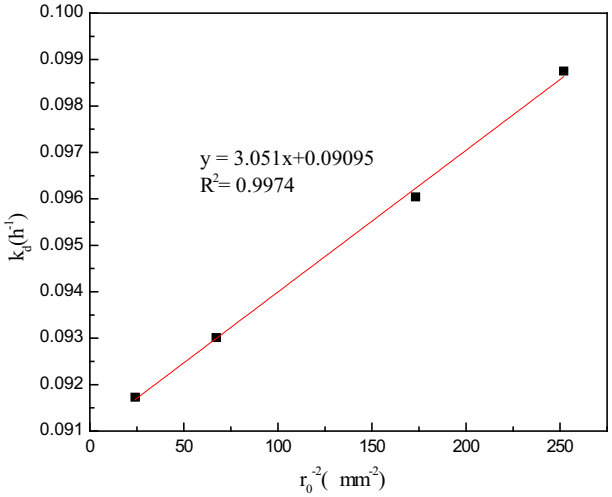

Figure 5 Relationship between rate constant and average initial particle size.

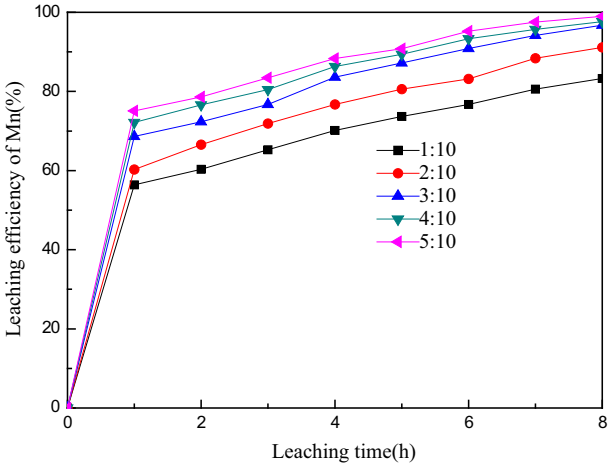

Figure 6 Effect of weight ratios of PAP to MDO on the leaching efficiency of manganese.

with R^2 of 0.9967 shown in Fig. 7. From k_d and each weight ratio, a plot of $\ln k_d$ versus $\ln C_w$ was obtained. The order of the reaction with respect to C_w was proportional to 1.25 ($C_w^{1.25}$) with R^2 of 0.9758 showing a strong dependency of the leaching efficiency of manganese on C_w.

3.5. Effect of sulfuric acid concentration

The effect of sulfuric acid concentrations (C_H) was studied by varying the initial C_H from 1.0–2.3 mol·L^{-1} under the same leaching conditions. Results are summarized in Fig. 8. Fig. 8 shows that the leaching efficiency increases as C_H is increased, due to the increase of C_H could enhance the leaching efficiency and the diffusion rate of the H^+, which increased the leaching efficiency of manganese. The increase in manganese leaching efficiency slowed when the sulfuric acid concentration exceeded 1.7 mol·L^{-1}. Higher concentration should be avoided due to the fact that concentrated sulfuric acid is consumed in attacking the gangue constituents of the ore. Thus, it is preferable to

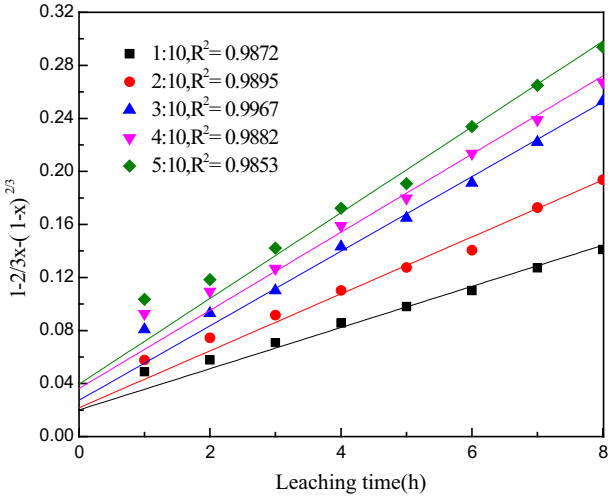

Figure 7 Relationship between $1-\frac{2}{3}X-(1-X)^{2/3}$ and leaching time at various weight ratios of PAP to MDO.

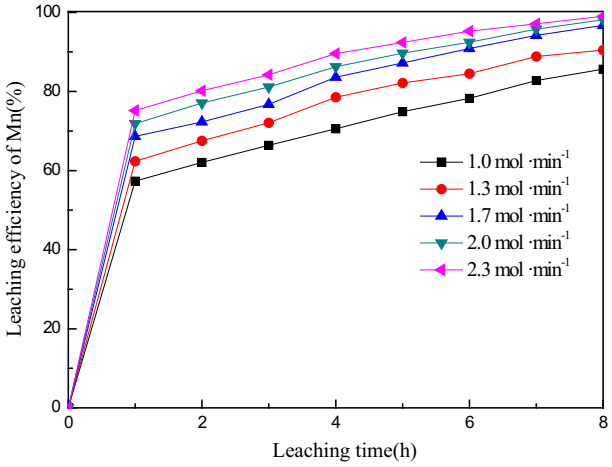

Figure 8 Effect of sulfuric acid concentration on the leaching efficiency of manganese.

apply the leaching process using 1.7 mol·L^{-1} sulfuric acid. The effect of C_H found in this investigation agrees well with the conclusions reported by Tekin et al. [18] and Su et al. [21]. The results were also applied to Eq. (1) and k_d values for each C_H were accordingly determined. The linear relationship between the reaction rate and C_H is well with R^2 of 0.9837 and this confirms again the reaction control mechanism by the inner diffusion. Similarly, a plot of $\ln k_d$ versus $\ln C_H$ shown in Fig. 9, the reaction order was determined to be 0.797 ($C_H^{0.797}$) with R^2 of 0.9950.

4. Reaction rate equation

The activation energy and the orders of reaction value with respect to particle size, C_H, and C_W follow the shrinking core model for the inner diffusion controlled process. According to Eq. (1), the apparent rate constant k_d can be expressed as follows:

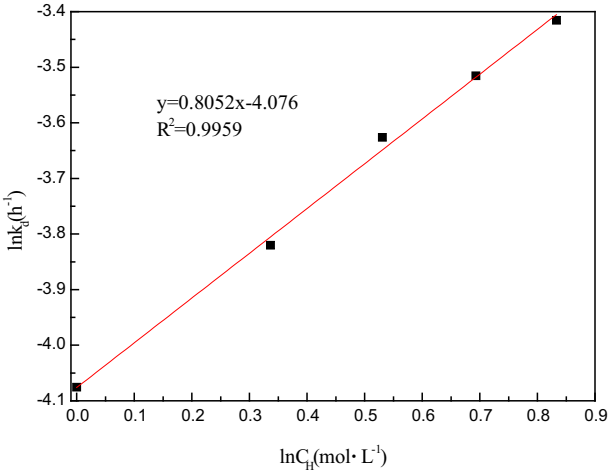

Figure 9 Plot for the determination of reaction order with respect to H_2SO_4 concentration.

$$K_d = \frac{k_0}{r_0^2} \times C_w^{1.25} \times C_H^{0.797} \times \exp\left(-\frac{15180}{RT}\right) \tag{5}$$

where k_0 is 607.77, which is calculated from the provided data in Figs., such as Fig. 3 and Fig. 7 [21]. Thus the semi-empirical kinetic leaching of manganese can be described by Eq. (6).

$$1-\frac{2}{3}X-(1-X)^{\frac{2}{3}} = \frac{607.77}{r_0^2} \times C_w^{1.25} \times C_H^{0.797} \times \exp\left(-\frac{15180}{RT}\right)t \tag{6}$$

To determine the adaptability of Eq. (6), the X values calculated by Eq. (6) were compared with that obtained from the experiments. The calculated conversions agree well with the experimental data with the relationship determined as the follows:

$$X_{cal} = 0.93112X_{exp} + 0.09174 \tag{7}$$

5. Conclusions

The reduction leaching kinetics of MDO with PAP in dilute sulfuric acid solution was investigated. The results reveal that the leaching rate increases gradually with the increase of H_2SO_4 concentration, weight ratio of *P. americana* branch powders to ores and leaching temperature and with the decrease of the size of particles. The kinetic analysis indicates that the leaching process follows shrinking core model and is controlled by diffusion through the insoluble layer of the associated minerals. The semi-empirical kinetic model was proposed. The apparent activation energy of 15.18 kJ·mol^{-1} also confirms the leaching process controlled by inner diffusion model. The exponents of 0.797 for sulfuric acid concentration and 1.25 for weight ratio of PAP to MDO were concluded.

Acknowledgments

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